



Adsorption and catalytic thermolysis of gaseous urea on anatase TiO₂ studied by HPLC analysis, DRIFT spectroscopy and DFT calculations

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ABSTRACT

High-purity gaseous urea was generated by passing a carrier gas at 100 °C through an inert cordierite monolith impregnated with urea, and the gaseous urea adsorbed onto anatase TiO₂ catalyst samples. Urea adsorption on the catalysts was confirmed by two independent methods: high performance liquid chromatography (HPLC) analysis and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Moreover, urea adsorption at the anatase (101) surface was studied by density functional theory (DFT) calculations. In combination with the DRIFT spectra, the DFT calculations indicated that two different adsorbed states of deprotonated urea were present on the catalyst simultaneously: in one adsorbed state, urea bound at one Ti site, and in the other adsorbed state urea was rotated and bound at two Ti sites. The confirmation of urea adsorption on anatase supports our previous finding that urea thermolysis is a catalytic reaction.

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1. Introduction

In the selective catalytic reduction (SCR) of NO_x in diesel vehicles, urea solution is dosed into the hot exhaust to produce the actual reducing agent, ammonia [1]. According to the established mechanism, urea first thermolyzes to yield ammonia and isocyanic acid (HNCO) in a non-catalytic reaction, and the intermediately formed HNCO is subsequently hydrolyzed on the SCR catalyst or on a dedicated hydrolysis catalyst [2]. However, a large fraction of the dosed urea remains unreacted before it enters the catalyst [1]. Therefore, the possibility that urea thermolysis is a catalytic reaction should also be considered.



In fact, scattered information in the literature indicates that urea thermolysis itself is catalyzed on metal oxide and SCR catalysts [3–6]. Recently, we have reported about catalytic urea thermolysis under steady-state conditions [7,8]. Our results clearly demonstrated the catalytic nature of this reaction, with anatase TiO₂ being

the most active catalyst among those tested. The activities exhibited the order TiO₂ > H-MFI > Al₂O₃ > ZrO₂ > SiO₂.

Larrubia et al. have studied the adsorption of urea onto a V₂O₅–MoO₃–TiO₂ SCR catalyst using transmission/absorption Fourier transform infrared spectroscopy [5]. They managed to adsorb gaseous urea on the catalyst surface; however, NH₃ and CO₂ were the main species in the gas phase. Significantly better results were obtained when a mixture of solid urea and catalyst powder was heated under vacuum to remove non-adsorbed bulk urea. As a result of heating, a characteristic peak of bulk urea (1454 cm⁻¹) disappeared, which indicated that only adsorbed urea and decomposition products remained in the sample. The spectra of the adsorbed urea showed a strong new band at 1562–1552 cm⁻¹, which was attributed to the asymmetric OCN stretching mode of adsorbed urea. Hence, Larrubia et al. proposed that urea adsorbs in its anionic form, as shown in Fig. 1 [5].

In the present study, we recorded diffuse reflectance infrared Fourier transform (DRIFT) spectra of urea adsorbed onto an anatase TiO₂ catalyst. DRIFT samples were prepared via the adsorption of high-purity gaseous urea onto the catalyst. Catalyst samples were washed, and the washing solutions were analyzed using high performance liquid chromatography (HPLC) to independently confirm urea adsorption of the urea. To investigate how urea adsorbs, we performed density functional theory (DFT) calculations of urea adsorbed at the anatase TiO₂ (101) surface.

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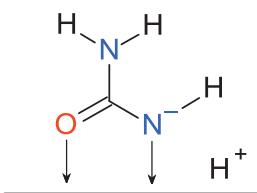


Fig. 1. Adsorbed urea in its anionic form, as proposed by Larrubia et al. [5].

2. Experimental and theoretical details

2.1. DRIFT samples and catalyst coating

DRIFT samples were prepared via three different methods:

- Adsorption of gaseous urea onto anatase TiO_2 catalyst powder (Crystal Global DT-51), see Section 2.2. Abbreviation: "urea (g)". Additionally, NH_3 was adsorbed onto TiO_2 . Before adsorbing NH_3 , the TiO_2 sample was cleaned at 450°C inside the DRIFT cell, then the temperature was set to 60°C and the DRIFT cell was supplied with 200 ppm NH_3 in N_2 for 75 min.
- Mixing of urea solution with catalyst powder by sonication for 3 min, followed by drying under ambient conditions. Abbreviation: "urea (aq)". For comparison, TiO_2 samples with biuret, cyanuric acid, ammelide and melamine were prepared likewise. Ammelide was suspended at 0.1% concentration.
- Dry grinding of solid urea (Merck, $\geq 99.5\%$ purity) with catalyst powder, CaF_2 (Sigma-Aldrich, puriss.), KBr (Fluka, $>99\%$ purity) or cordierite (Corning). Abbreviation: "urea (s)".

The BET surface area of the anatase TiO_2 catalyst was $90 \text{ m}^2/\text{g}$, measured on a Quantachrome Autosorb 1-c instrument under relative pressures p/p_0 that ranged from 0.05 to 0.3. The particle size was $\bar{\Omega}\text{D}_{50} = 1.70 \mu\text{m}$, measured on a Horiba LA-950 laser diffraction particle analyzer [9].

In addition to catalyst powder, gaseous urea was also adsorbed onto a TiO_2 -coated cordierite monolith, which was prepared as described previously [9]. The monolith was coated with 0.6 g of TiO_2 (including 10% wt% commercial silicate binder, Ludox AS-40).

2.2. Adsorption and thermolysis of gaseous urea onto TiO_2

Gaseous urea was obtained by passing a carrier gas at 100°C and at atmospheric pressure through an inert cordierite monolith that was impregnated with urea. According to our previous study, urea desorbed from the monolith in monomolecular form [10]. The applied temperature of 100°C was expected to result in a urea concentration of 27 ppm in the gas phase (assuming saturation) [10,11]. Because of the low temperature applied, non-catalytic urea decomposition was negligible [10].

To perform urea adsorption, a sample of TiO_2 -catalyst powder was charged into a crucible and placed in the hot urea-containing carrier gas, as shown in Fig. 2. Because the TiO_2 catalyst was also exposed to the sublimation temperature of 100°C , urea had to adsorb onto the catalyst rather than condense into the

bulk form. Notably, at the reactor exit, where the temperature was lower, the urea vapor condensed and formed needle-shaped crystals.

Urea adsorption was performed in a tubular quartz reactor with an inner diameter of 28 mm. The setup has been described in detail elsewhere [10]. An inert cordierite monolith (400 cpsi, 40 mm long, 17.5 mm wide and 12.4 mm high) was impregnated with 430 mg of urea by dipping it into 40 wt% urea solution. The impregnated monolith was inserted into a metal adaptor and the metal adaptor was placed in the reactor. The N_2 carrier gas flow was set to 200 L/h at standard temperature and pressure (STP), which resulted in a GHSV of $23,000 \text{ h}^{-1}$ through the impregnated monolith. The impregnated monolith was first dried inside the reactor at 70°C , and the crucible with $\approx 0.1 \text{ g}$ of TiO_2 was subsequently placed in the metal adaptor, as shown in Fig. 2. In some of the experiments, a humid gas mixture composed of 3% H_2O , 10% O_2 and balance N_2 was used as the carrier gas instead of pure N_2 . Because drying of the impregnated monolith catalyst was not necessary in this case, the catalyst powder was placed in the reactor at the beginning.

In addition, we performed urea adsorption at 100°C and urea thermolysis at 130°C on TiO_2 -coated monoliths (20 mm long, other dimensions identical to those of the inert monolith) inserted into the metal adaptor instead of the crucible. Urea thermolysis on the TiO_2 -coated monolith was performed with a flow of 10% O_2 in N_2 at a rate of 431 L/h at STP ($\text{GHSV} = 98,000 \text{ h}^{-1}$).

2.3. HPLC analysis

To quantify the adsorbed urea and the eventual urea decomposition byproducts on the TiO_2 samples, we applied HPLC analysis using a Dionex UltiMate 3000 instrument equipped with an anion exchange column (Waters WAT026770 IC-PAK ANION HC 4.6×150) and a photodiode-array detector. A 5 mM sodium phosphate buffer solution adjusted to pH 10.4 was used as the eluent, which allowed the separation of the most important urea decomposition byproducts [10]. The UV absorption was measured at 5 wavelengths simultaneously: 192 nm for urea, 204 nm for melamine, 214 nm for cyanuric acid, 230 nm for ammelide and 197 nm for biuret and most of the other compounds. Liquid samples were obtained by washing a monolith or a sample of catalyst powder in the HPLC eluent overnight [9].

For the urea thermolysis experiment conducted at 130°C , gaseous urea and HNCO were absorbed out of the carrier gas by a liquid-quench probe [12,13] and then quantified by HPLC. Three liquid samples were collected sequentially at intervals of 5 min. The results are given in the form "average \pm standard deviation".

2.4. DRIFT measurements

DRIFT spectra were measured on a ThermoNicolet Nexus FTIR spectrometer at a resolution of 4 cm^{-1} using the Smart Collector and Environmental Chamber accessories. The Environmental Chamber is a heated DRIFT cell that is equipped with ZnSe windows and gas supply lines. The samples were placed in the sample holder and pressed and flattened with a spatula. The DRIFT cell was always purged with either pure N_2 (140 L/h at STP) or with a gas mixture composed of 3% water, 10% O_2 and balance N_2 (200 L/h at STP).

DRIFT spectra were measured at various temperatures up to 300°C . The measurements were started at low temperature, and the temperature was increased step-wise. All of the shown spectra are subtraction spectra. Background spectra of urea-free samples were recorded under dry N_2 at the same temperatures as the actual samples.

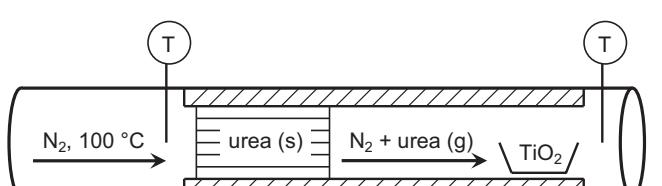


Fig. 2. Schematic of the experimental setup for urea evaporation and adsorption onto TiO_2 .

Table 1
HPLC analysis of catalyst and monolith washing solutions.

Sample	Carrier gas	Duration (h)	Urea/TiO ₂ (wt%)	Composition of compounds in washing solution, (wt%)					
				Urea	Biuret	Triuret	HNCO	Cyanamide	CYA
TiO ₂ powder	Dry N ₂	21.5	>1	94.0	5.9	0.1	0	0	0
TiO ₂ monolith	Dry N ₂	20.5	4.3	73.9	21.7	1.5	1.8	0.69	0.18
TiO ₂ monolith	3% H ₂ O	18	5.5	99.5	0.5	0	0	0	0.003
Inert monolith	Dry N ₂	21.5	110 mg	99.99	0	0.005	0	0	0.002

2.5. Computational details

The electronic structure of the Ti₈O₂₈H₂₄ cluster, which represents the (101) surface of anatase, and that of the urea adsorbates was calculated using ab initio DFT methods (StoBe code [14]). We chose to consider the (101) surface because it was found to be abundant based on high-resolution powder X-ray diffraction results (XRD) in another study [15]. The generalized gradient-corrected functionals according to Perdew, Burke and Ernzerhof (RPBE) were used to account for electron exchange and correlation [16,17]. All Kohn–Sham orbitals were represented by linear combinations of atomic orbitals (LCAOs) with Gaussian basis sets for the atoms [18,19]. The vibration frequencies were calculated by single-point energy calculations of the optimized geometries. The calculations of the vibrational frequencies were performed with harmonic approximations as well as with an anharmonicity fit in the Morse potential function, as implemented in the StoBe code [20].

3. Results and discussion

3.1. Confirmation of urea adsorption by HPLC analysis

Gaseous urea was adsorbed onto TiO₂ at 100 °C, as described in Section 2.2. Non-catalytic urea decomposition was negligible at 100 °C [10]; however, urea may have decomposed on the catalyst. To confirm that urea was present on the TiO₂ powder samples and to determine whether byproducts were formed, we performed HPLC analysis of catalyst washing solutions. After the adsorption of urea onto TiO₂ powder, part of the sample was used for DRIFT measurements. The remaining sample was washed in the aqueous HPLC eluent, and the washing solution was analyzed by HPLC. In addition, TiO₂-coated monoliths with adsorbed urea were analyzed likewise. Finally, the inert cordierite monolith that had been impregnated with urea and used as a source of urea vapor was analyzed after the experiment. Table 1 shows the results.

HPLC analysis of the catalyst washing solutions showed that urea was the main (water-soluble) constituent in all the TiO₂ samples. On the TiO₂ powder placed in the crucible and exposed under dry N₂, we found slightly more than 1 wt% of urea per TiO₂. In addition to 94% urea, 6% biuret was found in the washing solution. Apparently, some urea was catalytically thermolyzed on the TiO₂ surface to form HNCO, and the HNCO then reacted with intact urea to form biuret [3,9,21]. When a TiO₂-coated monolith was placed in the reactor instead of a crucible, more urea adsorbed onto the catalyst and more biuret (22%) was formed. Adsorption worked more efficiently on the monolith due to its significantly greater geometric surface area. The resulting greater surface coverage of urea on the TiO₂-coated monolith may explain the

increased biuret yield compared to that obtained with the powder. Because of its low vapor pressure [9], biuret was accumulated on the catalyst surface during the complete exposure time at 100 °C. In contrast to biuret, very little cyanuric acid was formed. We reported analogous results elsewhere [9], where we concluded that HNCO preferentially combines with urea rather than with biuret. Thermolysis produced significant amounts of cyanuric acid only when a catalyst-coated monolith was impregnated with biuret [9].

When urea was adsorbed from humid carrier gas, very little biuret was formed. In this case, HNCO hydrolyzed due to the presence of water instead of being consumed for biuret formation, or the formed biuret was hydrolyzed again [3,6,9,22,23]. Notably, the urea concentration of approximately 27 ppm was significantly lower than the water concentration of 30,000 ppm, and the catalyst still adsorbed a significant amount of urea. The adsorption of urea from the humid carrier gas indicated that urea adsorbs more strongly onto TiO₂ than does water.

Pure urea was found on the impregnated inert monolith that had been used as the source of urea vapor, which indicated that urea was stable at 100 °C in the absence of a catalyst. Of the initial amount of 430 mg urea, 110 mg remained on the monolith after it had been heated to 100 °C for 21.5 h. Hence, 430 mg – 110 mg = 320 mg urea had evaporated during the experiment. Based on the vapor pressure of urea [10,11], 310 mg of urea was expected to evaporate, which is in good agreement with the measured amount of remaining urea.

3.2. Quasi-stationary thermolysis of gaseous urea on a TiO₂-coated monolith

Quasi-stationary urea thermolysis over TiO₂ was performed at 130 °C using an impregnated inert monolith as the source of gaseous urea. Instead of the crucible shown in Fig. 2, a TiO₂-coated monolith was placed in the reactor downstream of the inert monolith. After approximately 30 min of equilibration at 130 °C, three liquid samples with absorbed product gas were collected during 3 × 5 min for HPLC analysis. For comparison, an analogous experiment was performed without a catalyst. Because of the catalytic activity of TiO₂, the HNCO yield increased from 5% to 35% (Table 2). The carbon balance in both cases agreed fairly well, which indicated that the catalyst was under stationary conditions.

Table 2 shows the results of solvent-free, catalytic thermolysis of gaseous urea. These results support our previous findings about catalytic urea thermolysis under steady-state conditions at various temperatures over different metal oxide catalysts [7,8]. As we have previously reported [7,8], urea was dosed in a borosilicate glass reactor in the form of a water-free organic solution by a gas-assisted spray nozzle. The spray aerosols appeared to evaporate upstream of the catalyst; however, the existence of urea aerosols at the catalyst

Table 2

Quasi-stationary decomposition of gaseous urea at 130 °C. Carrier gas: 10% O₂ in N₂, 431 L/h at STP.

1st monolith (GHSV, h ⁻¹)	2nd monolith (GHSV, h ⁻¹)	Urea (ppm)	HNCO (ppm)	Total carbon (ppm)
Inert (50,000)	TiO ₂ -coated (98,000)	119 ± 0.5	63 ± 2	181
Inert (50,000)	None	182 ± 9	8.6 ± 0.7	190

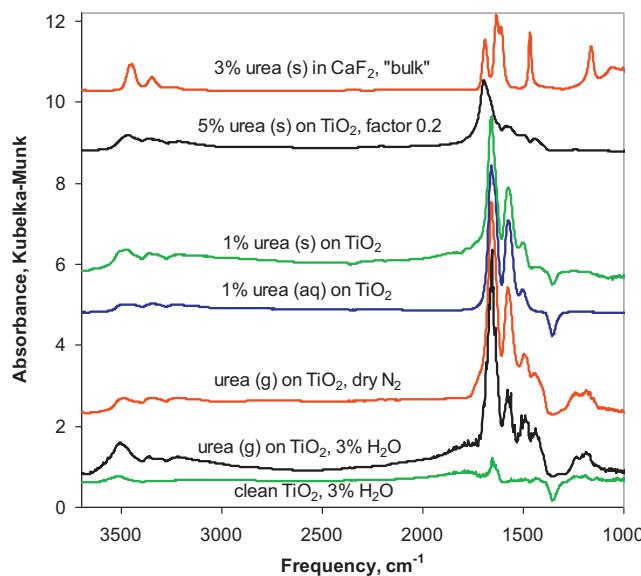


Fig. 3. DRIFT spectra of urea recorded at 80 °C; the intensities of the “5% urea (s) on TiO₂” sample were multiplied by a factor of 0.2. Sample preparation methods: urea (g)=urea vapor adsorbed onto catalyst powder at 100 °C; urea (aq)=aqueous urea solution mixed with catalyst powder by sonication, followed by drying under ambient conditions; urea (s)=solid urea mixed with catalyst powder by dry grinding.

entrance could not be excluded with certainty [7,8]. Additionally, a solvent was always used to dose the urea.

3.3. DRIFT measurements at 80 °C

Fig. 3 shows the DRIFT spectra of urea on TiO₂ recorded at 80 °C. A temperature of 80 °C was chosen to desorb weakly adsorbed water without inducing urea decomposition. The spectrum of urea in CaF₂ and that of clean TiO₂ under humid gas are shown for comparison. The latter spectrum was the “ads. urea on TiO₂” sample after in situ cleaning by hydrolysis at 450 °C. The bottom two spectra in Fig. 3 were recorded under humid model gas; all the other spectra were recorded under dry N₂. The spectrum of urea in CaF₂ best represented bulk solid urea because it showed better-defined peaks compared to the spectra of urea in KBr or urea in cordierite powder (not shown). Furthermore, our spectrum of urea in CaF₂ agrees best with the spectrum of pure crystalline urea measured by Grdadolnik and Maréchal, who used attenuated total reflectance (ATR) spectroscopy [24].

We attributed the bands of our 3% urea in CaF₂ spectrum using the assignments of Grdadolnik and Maréchal [24], see Table 3. In their study, the absorption bands were assigned based on a comparison of the spectra from different isotopomers of urea (urea with D and/or ¹³C) [24]. Here, the bands at 1689 cm⁻¹ and 1631 cm⁻¹ were attributed to the NH₂ bending vibrations, the band at 1608 cm⁻¹ was attributed to the C=O stretching vibration, the band at 1465 cm⁻¹ was attributed to the CN stretching vibration, and the band at 1160 cm⁻¹ was attributed to the NH₂ rocking vibration (Table 3).

The spectra of adsorbed urea strongly differed from that of the bulk urea spectrum (see 1% urea (s) on TiO₂, 1% urea (aq) on TiO₂, urea (g) on TiO₂ vs. bulk urea in Fig. 3). In the 1% urea (aq) on TiO₂ spectrum, the two prominent peaks of bulk urea at 1465 cm⁻¹ (CN stretching vibration) and at 1160 cm⁻¹ (NH₂ rocking vibration) disappeared. On the other hand, new and/or shifted peaks appeared at 1657 cm⁻¹, 1573 cm⁻¹ and 1501 cm⁻¹. This change in the urea spectrum is in good agreement with the results reported by Larrubia et al. [5]. The peak assignment of adsorbed urea is discussed in the next section.

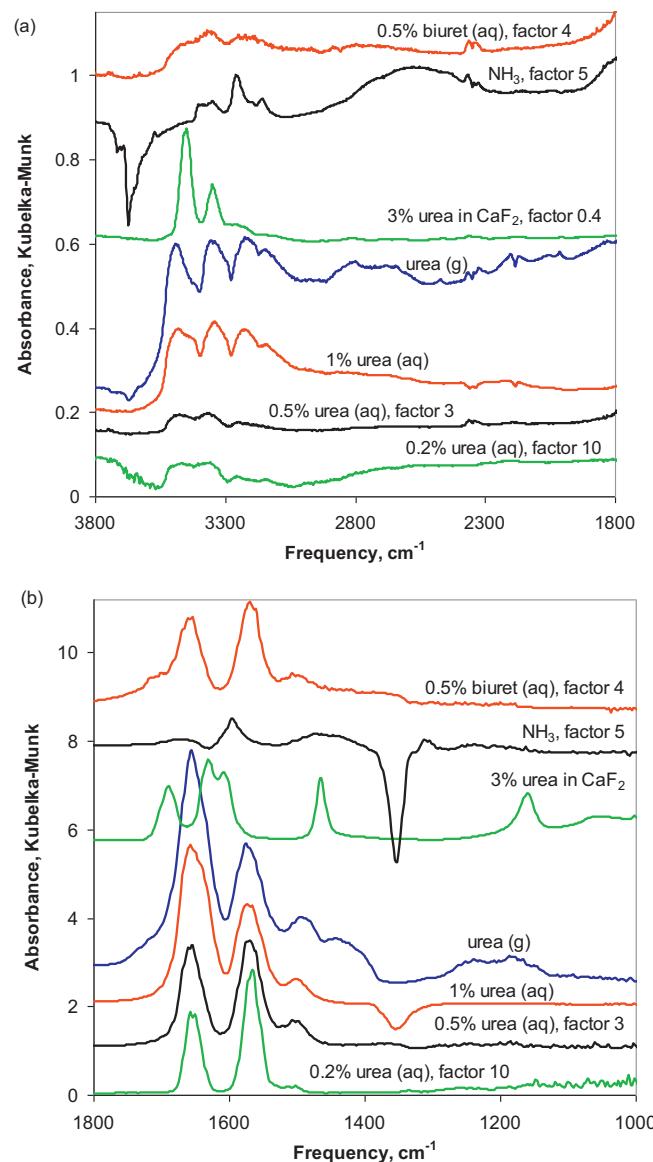


Fig. 4. DRIFT spectra of different urea on TiO₂ samples, of biuret on TiO₂ and of NH₃ on TiO₂. All spectra were recorded at 80 °C. NH₃ was adsorbed onto TiO₂ by supplying the DRIFT cell with 200 ppm NH₃ in N₂ at 60 °C for 75 min. The shown NH₃ on TiO₂ spectrum was recorded at 80 °C, 20 min after switching to purging with pure N₂.

Interestingly, the three different preparation methods for the urea on TiO₂ samples resulted in quite similar spectra (see 1% urea (s) on TiO₂, 1% urea (aq) on TiO₂ and urea (g) on TiO₂ in Fig. 3). Apparently, urea (aq) predominantly adsorbed onto the same sites of TiO₂ as did gaseous urea. Also, the grinding of solid urea with the catalyst seemed to provide sufficient energy to induce urea diffusion to the same energetically favored adsorption sites of TiO₂. However, a clearly different spectrum was obtained when 5 wt% instead of 1 wt% of urea was ground with TiO₂: the 5% urea (s) on TiO₂ spectrum appeared to be a transition from the spectrum of 1% urea on TiO₂ to that of bulk urea. The most intense peak in the spectrum of 5% urea (s) on TiO₂ was located at 1695 cm⁻¹, which matches well with the peak at 1689 cm⁻¹ (NH₂ bending vibration) in the spectrum of bulk urea. The spectrum of 5% urea (s) on TiO₂ did not show other prominent peaks at wavenumbers less than 1800 cm⁻¹, but the two most intense peaks in the spectrum of the 1% urea (aq) on TiO₂ at 1655 cm⁻¹ and 1575 cm⁻¹ seemed to be present as shoulders in the spectrum of 5% urea (s) on TiO₂. The

Table 3

Comparison of the vibration frequencies [cm^{-1}] of urea in different samples with the DFT-calculated results (represented in italics) obtained in the present work (p.w.) or with results taken from the literature.

Urea sample	νNH_2	δNH_2	νCO	$\nu_{\text{as}} \text{Ti—OCN—Ti}$	$\delta \text{HN—C—NH}$	νCN	ρNH_2	δNH	Method, source
3% urea (s) in CaF_2 , 80°C	3447, 3349	1689, 1631 ^a	1608			1465, 1008	1160, 1051		DRIFT, p.w.
Crystalline urea	3437 ^a , 3343	1682, 1624	1599			1466, 1003	1156, 1057		ATR [24]
<i>Adsorbed urea form A</i>	3603, 3479, 3465	1638 ^a		1578	1438	1002	1102	1198	DFT, p.w.
<i>Adsorbed urea form B</i>	3565, 3523 (NH_2), 3423, 3393 (NH)	1638		1579	1375 ^a	966	1091	1221	DFT, p.w.
Urea (g) on TiO_2 , 80°C	3488, 3353, 3224	(1635)	1655 ^a	1575 (1567), (1560)	1492, 1443	1240	1185	1240	DRIFT, p.w.
1% urea (aq) on TiO_2 , 80°C	3480, 3341, 3231	(1637)	1657 ^a	1573 (1566), (1556)	1501				DRIFT, p.w.
0.5% urea (aq) on TiO_2 , 80°C	3469, 3355, 3250	(1638)	1654	1569 ^a (1560)	1506				DRIFT, p.w.
0.2% urea (aq) on TiO_2 , 80°C				1557 (1651)	1566 ^a , (1556)	1502			DRIFT, p.w.
0.1% urea (aq) on TiO_2 , 80°C				1653	1568 ^a	1507			DRIFT, p.w.
1% urea (aq) on V-Mo-TiO_2	3469, 3365, 3250		1652 ^a	1562–1552					FTIR [5]
<i>Gaseous urea</i>	3584–3455	1624	1752 ^a				1372		DFT [10]
<i>Gaseous urea</i>	3540, 3437	1600	1773 ^a				1392		FTIR [10]

In brackets: shoulder.

^a Most intensive peak.

spectrum of 5% urea (s) on TiO_2 may be explained by the relatively high surface coverage.

The presence of water in the purge gas of the DRIFT cell (urea (g) on TiO_2 , 3% H_2O in Fig. 3) caused the superposition of the urea spectrum with numerous small, narrow water signals. Apart from the small water signals, the urea spectrum did not appear to be influenced by the presence of water in the purge gas. We attempted to correct the urea spectrum by subtracting the spectrum of clean TiO_2 acquired under humid model gas but did not obtain a satisfactory result. Nonetheless, the humid purge gas substantially influenced the spectra when the temperature was increased greater than 100°C because the NCO band at 2200 cm^{-1} was suppressed by HNCO hydrolysis.

Although the spectra of urea (g) on TiO_2 and 1% urea (aq) on TiO_2 in Fig. 3 were quite similar, a closer look reveals some differences, see also Fig. 4. The spectrum of urea (g) showed small peaks at 1443 cm^{-1} , 1240 cm^{-1} and 1185 cm^{-1} , which were not observed in the urea (aq) samples (Fig. 4b). Since the urea (g) on TiO_2 sample was contaminated with biuret that had formed during urea adsorption at 100°C (see Table 1), the additional peaks in urea (g) might be attributed to biuret. Also, NH_3 , which was not quantified by our HPLC method, may have contributed to the urea (g) on TiO_2 spectrum. However, the 0.5% biuret (aq) and the NH_3 on TiO_2 spectra (top two curves in Fig. 4b), did not show peaks at 1443 cm^{-1} , 1240 cm^{-1} or 1185 cm^{-1} , indicating that these peaks were attributed to adsorbed urea. We assume that the urea distribution on the catalyst surface was more uniform in the urea (g) on TiO_2 sample than in the urea (aq) on TiO_2 samples, which allowed the observation of additional peaks.

The negative peak at 1354 m^{-1} in the NH_3 on TiO_2 spectrum in Fig. 4b was attributed to a breaking of Ti—O—S bonds upon interaction with NH_3 . Hauck et al. observed a similar negative peak at 1371 cm^{-1} [22]. Sulfate species are present in commercial TiO_2 because of its synthesis via the sulfate method, and the sulfate species show a characteristic band in this region due to their S=O stretching vibration [22]. Our 1% urea (aq) on TiO_2 spectrum in Fig. 4b and in Fig. 3 also showed a negative peak at the same position, but that peak was smaller.

Fig. 4 also compares urea (aq) on TiO_2 samples with different urea concentrations. Decreasing the urea concentration changed the relative intensities of the peaks. (At 1% urea concentration, the peak at 1657 cm^{-1} was most intense, but at lower concentrations of 0.5%, 0.2% and 0.1% (0.1% not shown), the peak at 1569 cm^{-1} became most intense). Further, the relative intensity of the peak at 1501 cm^{-1} (compared to the most intense peak) decreased at

low urea concentrations. Anyway, the peaks of urea (g) on TiO_2 at 1443 cm^{-1} , 1240 cm^{-1} and 1185 cm^{-1} were not observed in any of the urea (aq) on TiO_2 samples.

3.4. Comparison of DRIFT measurements with DFT calculations

Table 3 shows a comparison of the vibration frequencies of urea in different samples, and the DFT-calculated frequencies. The TiO_2 cluster with adsorbed urea, shown in Fig. 5, was used for the DFT calculations.

Fig. 5 shows the two different adsorption positions of urea at the anatase TiO_2 (101) surface that were found to be most likely. Adsorbed urea A (Fig. 5a) was deprotonated to the anionic form, $\text{HN}^-\text{C(O)NH}_2$, by proton transfer to surface O(2), and bound with the HN^- group at one Ti site with an adsorption energy of -0.26 eV . Adsorbed urea B (Fig. 5b) was similarly deprotonated and bound at two Ti sites with both the HN^- group and the double-bonded O, with an adsorption energy of -0.28 eV . Notably, adsorbed urea B corresponds to the scheme of adsorption proposed by Larrubia et al. [5]. We also considered zwitterionic urea, $\text{H}_2\text{NC(O}^+\text{H)}\text{N}^-\text{H}$, bound with the HN^- group at one Ti site with an adsorption energy of -0.78 eV . However, the zwitterionic form should have shown a strong OH stretching vibration band at 2539 cm^{-1} , which was not observed in the DRIFT spectra.

Fig. 6 shows a comparison between the experimental DRIFT spectra of urea adsorbed onto TiO_2 (with urea added in aqueous form in Fig. 6a and with urea in gaseous form in Fig. 6b) and the DFT-calculated frequencies. Fig. 6 focuses on the region below 1800 cm^{-1} , because both the experimental and the theoretical spectra showed only peaks with low intensity at higher wavenumbers. Comparison of the urea (g) on TiO_2 spectrum with the DFT-calculated spectra (Fig. 6b) indicates that the two different adsorbed states of urea shown in Fig. 5 exist on TiO_2 simultaneously. The two most intense peaks in the experimental spectra are in good agreement with the DFT calculations.

A closer examination of the most intense peak in Fig. 6b at 1655 cm^{-1} reveals a shoulder at approximately 1635 cm^{-1} , which indicates two overlapping peaks. Based on the calculated intensities, we attributed the main peak to the NH_2 bending mode of adsorbed urea A (measured: 1655 cm^{-1} , calculated: 1638 cm^{-1}) and the shoulder to the NH_2 bending mode of adsorbed urea B (measured: 1635 cm^{-1} , calculated: 1638 cm^{-1}).

The second-most intense peak was measured at 1575 cm^{-1} . This peak was attributed to the asymmetric Ti—OCN—Ti stretching modes of adsorbed urea A and B, which were calculated to occur

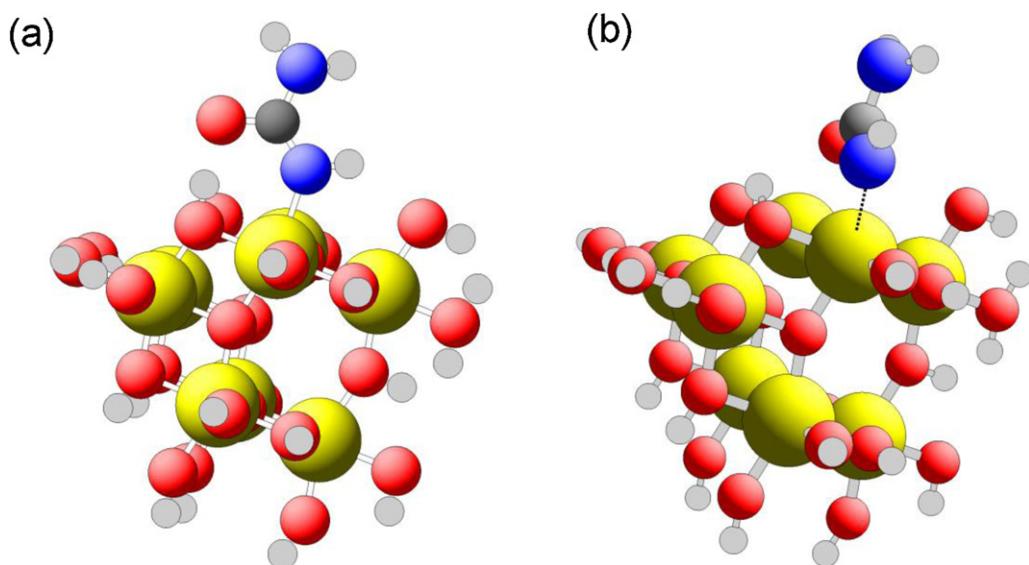


Fig. 5. Urea adsorbed onto the $\text{Ti}_8\text{O}_{28}\text{H}_{24}$ cluster, which represents the (101) TiO_2 surface; these results were used for the DFT calculations; (a): adsorbed urea form A; (b): adsorbed urea form B.

at 1578 cm^{-1} and 1579 cm^{-1} , respectively. Larrubia et al. observed a similar peak in the spectrum of urea on a $\text{V}_2\text{O}_5\text{--MoO}_3\text{--TiO}_2$ SCR catalyst at $1562\text{--}1552 \text{ cm}^{-1}$, which they considered to be characteristic for adsorbed urea [5]. They also assigned their peak at $1562\text{--}1552 \text{ cm}^{-1}$ to the asymmetric Ti--OCN--Ti stretching mode [5].

The next most intense peaks in the urea (g) on TiO_2 spectrum (Fig. 6b) were measured at 1492 cm^{-1} and 1443 cm^{-1} . These peaks were attributed to the HN--C--NH scissoring modes of adsorbed

urea A (measured: 1492 cm^{-1} , calculated: 1438 cm^{-1}) and of adsorbed urea B (measured: 1443 cm^{-1} , calculated: 1375 cm^{-1}). Further, the small peak at 1240 cm^{-1} was attributed to a combination of the NH bending of adsorbed urea A at 1198 cm^{-1} and to the CN stretching mode of adsorbed urea B at 1221 cm^{-1} . The nearby peak at 1185 cm^{-1} was assigned to the NH_2 rocking modes of adsorbed urea A and B at 1102 cm^{-1} and 1091 cm^{-1} , respectively.

Notably, the peaks at 1443 cm^{-1} , 1240 cm^{-1} and 1198 cm^{-1} were not observed in the urea (aq) on TiO_2 (Fig. 6a) or in the urea (s) on TiO_2 (Fig. 3) spectra, which is tentatively explained by interaction between adsorbed urea molecules. Interactions between adsorbed molecules reduce their degree of freedom, which can suppress some theoretically observed vibrations like bending of NH groups. By contrast, only single molecules adsorbed onto the TiO_2 surface with full degree of freedom were considered in our DFT calculations, which corresponds to a small coverage and an even distribution of urea at surface. Apparently, the urea was uniformly distributed in the urea (g) on TiO_2 sample and its DRIFT spectrum could therefore be well represented by the DFT calculations (Fig. 6b).

3.5. Urea thermolysis followed by DRIFT spectroscopy

Fig. 7 shows DRIFT spectra measured during the decomposition of (a) 1% and (b) 5% urea on TiO_2 . The urea was decomposed on the catalysts by increasing the temperature of the DRIFT cell stepwise (spectra were recorded at constant temperature). The spectra of the sample with the lower urea concentration of 1%, shown in Fig. 7a, remained substantially unchanged up to 150°C . At 200°C , most of the urea was decomposed. A close examination of the spectra (window with enlarged viewing in Fig. 7a) reveals a tiny peak that appeared at 2202 cm^{-1} at 100°C , which was assigned to the asymmetric stretching vibrations of adsorbed NCO groups [5,22,23,25] produced by the catalytic thermolysis of urea into HNCO and NH_3 [5,7,8]. The peak became more intense and shifted slightly to 2200 cm^{-1} at 120°C and to 2197 cm^{-1} at 150°C , where its intensity reached a maximum; however, the maximum-intensity peak was still significantly less intense than the peaks in the region of $1700\text{--}1500 \text{ cm}^{-1}$. After 9 min at 150°C , the intensity of the NCO peak decreased again, and it disappeared completely at 250°C . Possibly, only a small amount of NCO could build up at the

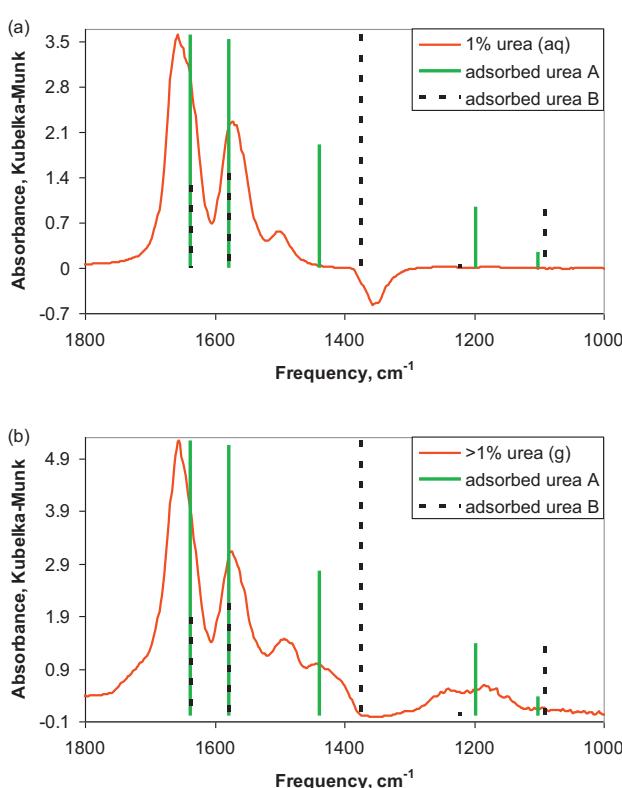


Fig. 6. Comparison of DRIFT spectra with DFT-calculated frequencies and intensities (vertical lines) for the two adsorbed states shown in Fig. 5 (a) 1% urea (aq), (b) $>1\%$ urea (g).

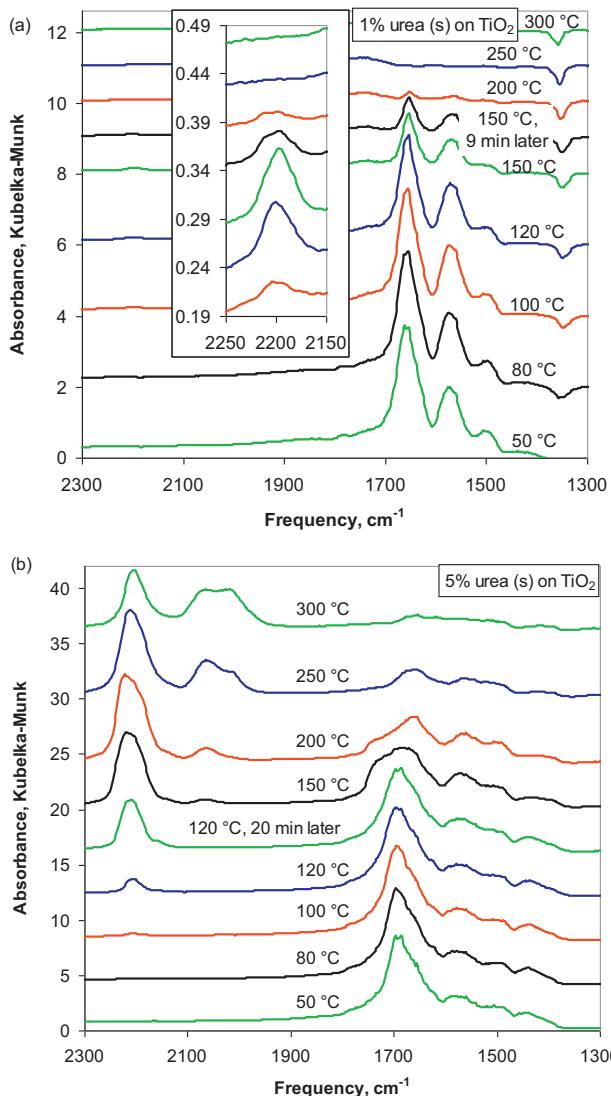


Fig. 7. DRIFT spectra measured during the decomposition of urea on TiO_2 : (a) 1% urea and (b) 5% urea.

catalysts surface because it was steadily hydrolyzed with adsorbed water.

Fig. 7b shows DRIFT spectra measured during the decomposition of 5% urea on TiO_2 . As previously mentioned in the discussion of Fig. 3, an increase in the urea concentration from 1% to 5% significantly changed the spectrum. We interpreted this behavior to be caused by a high surface coverage, which resulted in a spectrum with features of both bulk and adsorbed urea without simply being the sum of these two spectra. In analogy with the results reported by Larrubia et al. [5], heating the sample may desorb/decompose excessive urea so that a spectrum of adsorbed urea plus the decomposition products was observed at a certain temperature. Indeed, the three main peaks of adsorbed urea at 1657 cm^{-1} , 1573 cm^{-1} and 1501 cm^{-1} (Table 3) were observed in the spectrum of 5% urea on TiO_2 at $200\text{ }^\circ\text{C}$, with small shifts to 1654 cm^{-1} , 1560 cm^{-1} and 1506 cm^{-1} (Fig. 7b). Biuret probably was present as well, the pure biuret spectrum showed peaks at 1653 , 1570 (most intensive), 1506 cm^{-1} (Fig. 4b).

The decrease in the intensity of the largest peak at 1695 cm^{-1} (the NH_2 bending mode of bulk urea) upon heating was accompanied by the growth of several new peaks due to urea decomposition products and byproducts. Most importantly, isocyanate formation

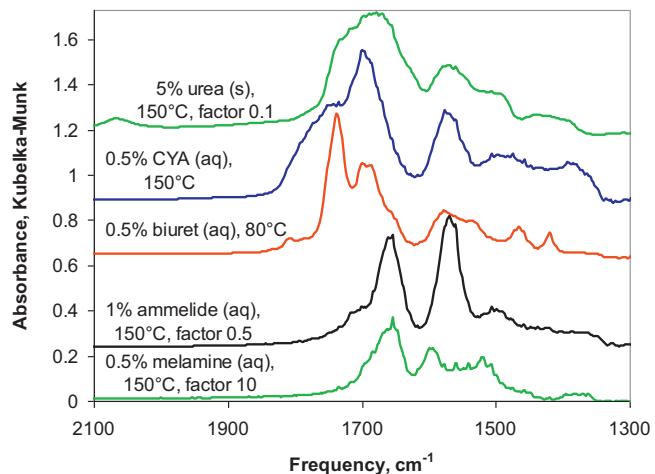


Fig. 8. Comparison between "5% urea (s) on TiO_2 ", taken from Fig. 7, and the spectra of the urea decomposition byproducts cyanuric acid (CYA), biuret, ammelide and melamine (from top to bottom) on TiO_2 .

was observed at the catalyst surface that showed peaks at 2204 – 2222 cm^{-1} . The high intensity of the NCO band (Fig. 7b), which is in contrast to the low-intensity band obtained with the 1% urea (s) on TiO_2 (Fig. 7a), was a consequence of the increased urea-to-water ratio. The use of 5% instead of 1% solid urea in the catalyst sample did not increase the amount of adsorbed water on the catalyst; hence, the major fraction of the HNCO could not be hydrolyzed.

At $150\text{ }^\circ\text{C}$, a new band appeared at 2066 cm^{-1} in the DRIFT spectrum (see Figs. 7b and 8), which we assigned, based on the work of Hauck et al. [22], to cyanamide adsorbed in the tautomeric and deprotonated form $-\text{N}=\text{C}=\text{NH}$. Cyanamide is the monomer of melamine and can be formed by the disproportionation of HNCO into CO_2 and cyanamide [26]. Cyanamide was also detected by HPLC (Table 1).

Furthermore, a shoulder at 1740 cm^{-1} was observed in the spectra of 5% urea on TiO_2 at 150 and $200\text{ }^\circ\text{C}$, which we tentatively assigned to the $\text{C}=\text{O}$ stretching mode of cyanuric acid (IUPAC name: 1,3,5-triazinane-2,4,6-trione) in its trione tautomeric form. A DFT vibration analysis of gaseous cyanuric acid showed bands at 1778 cm^{-1} , 1766 cm^{-1} and 1764 cm^{-1} for this mode. The assignment of the shoulder at 1740 cm^{-1} to cyanuric acid is supported by the spectrum of cyanuric acid on TiO_2 shown in Fig. 8. Further, Fig. 8 suggests that ammelide (IUPAC name: 6-amino-1,3,5-triazine-2,4-diol) also contributed to the shoulder with its most intense peak at 1737 cm^{-1} (Fig. 8).

At $250\text{ }^\circ\text{C}$, the band at 1740 cm^{-1} was no longer evident, which may be due to catalytic cyanuric acid de-polymerization into HNCO. This temperature is in fair agreement with the start of HNCO emissions between 250 and $275\text{ }^\circ\text{C}$ in a temperature programmed thermolysis experiment of cyanuric acid on TiO_2 [9]. Another possible explanation for the disappearance of the cyanuric acid shoulder (1740 cm^{-1}) at $250\text{ }^\circ\text{C}$ is the substitution of OH groups in cyanuric acid or ammelide with NH_3 , which yields ammeline (IUPAC name: 4,6-diamino-1,3,5-triazin-2-ol) or melamine (IUPAC name: 1,3,5-triazine-2,4,6-triamine).

The disappearance of the cyanuric acid shoulder (1740 cm^{-1}) at $250\text{ }^\circ\text{C}$ was accompanied by the growth of a new band at 2019 cm^{-1} , which we could not assign.

4. Conclusions

Gaseous urea was found, using HPLC analysis and DRIFT spectroscopy, to adsorb onto anatase TiO_2 at $100\text{ }^\circ\text{C}$. DFT calculations

suggested two different adsorbed states of deprotonated urea, $\text{HN}^-\text{C(O)NH}_2$, to be present at the anatase (101) surface: in one state, urea bound at one Ti site with an adsorption energy of -0.26 eV , and in the other state, urea was rotated and bound at two Ti sites with an adsorption energy of -0.28 eV . Zwitterionic urea, $\text{H}_2\text{NC(O}^+\text{H})\text{N}^-\text{H}$, was also considered but abandoned, because the expected OH vibration was not observed in the DRIFT spectra. The confirmation of urea adsorption supports our previous conclusion that catalytic urea thermolysis is the rate-determining step in the overall urea hydrolysis reaction on anatase TiO_2 to yield NH_3 and CO_2 , see refs [8,27].

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